Microwave Spectrum, Conformational Equilibrium, Intramolecular Hydrogen Bonding and Centrifugal Distortion of 3-Aminopropionitrile

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The microwave spectrum of 3-aminopropionitrile, $CH_2NH_2CH_2CN$, has been investigated in the 18.0−32.0 GHz spectral region at 0 °C. The two $C-C-C-N$ *gauche* conformations denoted I and II and shown in Fig. 1, were assigned. Both these rotamers are stabilized by an intramolecular hydrogen bond formed between the amino group hydrogen atom and the cyano group. The energy difference between I and II is 0(2) kJ/mol. The two identified conformations are each at least 4 kJ/mol more stable than any one of the three further forms shown in Fig. 1.

The $C-C-C-N$ dihedral angles are 63(3)° from *syn* in I and 59(3)° from *syn* in II, respectively. The $C-C-NH_2$ angle has a "normal" value of 108.0(15)° in I, while this angle opens up to 114.0(15)° in II. The angle between the $N-H$ bond involved in hydrogen bonding and the cyano group is about 4° from being parallel in both rotamers.

One vibrationally excited state was found for I, while two such states were identified for II. Accurate centrifugal distortion constants were determined for II and used to determine the $C-C$ torsional frequency as 100(10) cm^{-1} for this conformation.

The amino group may act as proton donor in molecules capable of forming weak internal hydrogen bonds. Several such amines have recently been studied by microwave spectroscopy. These studies include $CF_3CH_2NH_2$,[1] H_2NCH_2CN,[2] $H_2NCH_2C\equiv CH$,[3] $CH_2NH_2CH_2NH_2$,[4] CH_2NH_2COOH,[5] $CH_3OCH_2CH_2NH_2$,[6] $CH_2FCH_2NH_2$[7] and $CHF_2CH_2NH_2$.[8]

Amines may use both amino group hydrogen atoms in hydrogen bond formation. More than one hydrogen-bonded conformation may thus exist in most cases. Two hydrogen-bonded rotamers involving the amino group acting as proton donor have been assigned in the cases of $CH_2NH_2CH_2NH_2$[4] and $CH_2NH_2CH_2F$,[7] while three hydrogen-bonded conformations were found for $CHF_2CH_2NH_2$.[8] In the remainder of the above cited molecules, only one hydrogen-bonded rotamer where the amino group acts as proton donor, has been identified in each case.

3-Aminopropionitrile, $CH_2NH_2CH_2CN$, has five different all-staggered conformational possibilities as shown in Fig. 1. Conformations I and II each possesses an intramolecular hydrogen bond, whereas this interaction is not possible in the other three cases. This work was undertaken in order to see which of the five conformations of $CH_2NH_2CH_2CN$ are favoured. It was found that rotamers I and II, which are stabilized by weak hydrogen bonds formed between the amino group hydrogen atoms and the cyano group, are preferred by the molecule. The energy difference between I and II is 0(2) kJ/mol. No further conformations were identified. The hydrogen bond is so strong in each of I and II that they both are more stable than any one of III, IV and V by at least 4 kJ/mol.

EXPERIMENTAL

3-Aminopropionitrile was purchased from K&K Laboratories. The molecule was difficult to
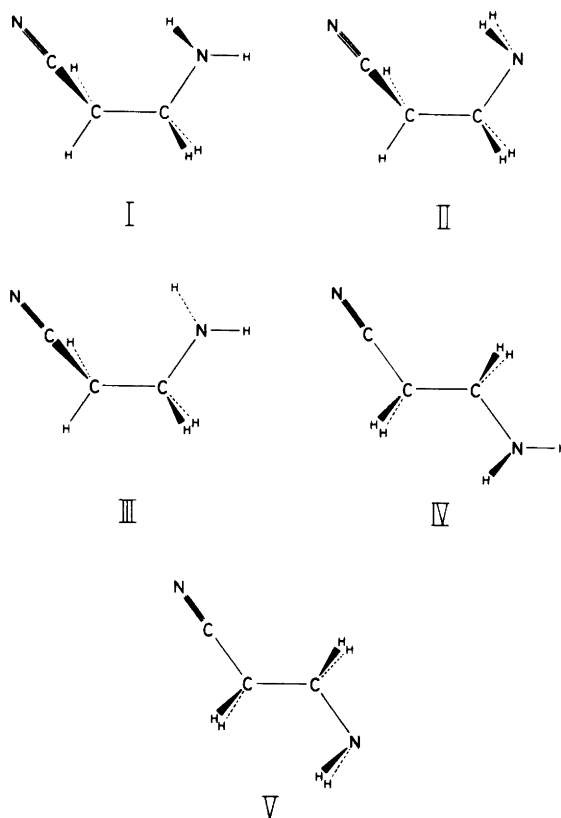
Fig. 1. Possible conformations of $CH_2NH_2CH_2CN$ with all-staggered atomic arrangements. I and II, both containing intramolecular hydrogen bonds, were assigned and the energy difference between them determined to be 0(2) kJ/mol. I and II are each at least 4 kJ/mol more stable than any one of III, IV or V.

handle because decomposition and/or polymerization reactions frequently occurred even during the registration of the microwave spectra where the compound was kept in a brass cell at a pressure of a few tenths of a pascal and a temperature of about 0 °C. Attempts to purify the compound by gas chromatography were unsuccessful because of polymerization reactions in the columns. The compound was kept at liquid nitrogen temperature when not in use, but decomposition/polymerization was always observed when the sample tubes were heated to room temperature in order to yield fresh samples. Ammonia appeared to be one decomposition product, but no further decomposition products were identified by their microwave spectra.

The spectrum was recorded on a conventional spectrometer in the 18–32 GHz spectral range. The spectrum was quite weak. The strongest lines appeared to have roughly 2×10^{-7} cm^{-1} intensity under these somewhat unfavourable experimental conditions. The cell could not be cooled below 0 °C because of insufficient vapour pressure of $CH_2NH_2CH_2CN$.

RESULTS

Assignment of conformation I. Preliminary rotational constants of I were computed using structural data taken from related molecules. Bond moment calculations using the values of Ref. 9 yielded $\mu_a = 3.0$ D, $\mu_b = 1.6$ D, and $\mu_c = 0.4$ D. The relatively strong *a*-type *R*-branch $J = 3 \rightarrow 4$ and $J = 4 \rightarrow 5$ transitions were therefore searched for and identified by their partially resolved Stark effects and rigid rotor fit. The assignments were

Table 1. Microwave spectrum of the ground vibrational state of conformation I of $CH_2NH_2CH_2CN$.

Transition	Observed frequency [a] (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion (MHz)
$2_{1,1} \rightarrow 3_{1,2}$	19391.27	−0.09	−0.48
$3_{1,3} \rightarrow 4_{1,4}$	23393.96	−0.03	−0.42
$3_{0,3} \rightarrow 4_{0,4}$	24313.71	0.06	−0.82
$3_{2,2} \rightarrow 4_{2,3}$	24646.91	0.06	−0.30
$3_{2,1} \rightarrow 4_{2,2}$	25008.11	0.11	−0.53
$4_{1,4} \rightarrow 5_{1,5}$	29181.85	−0.02	−0.94
$4_{0,4} \rightarrow 5_{0,5}$	30142.79	0.02	−1.43
$4_{2,3} \rightarrow 5_{2,4}$	30761.82	0.04	−1.03
$4_{2,2} \rightarrow 5_{2,3}$	31461.44	−0.04	−1.65
$4_{1,3} \rightarrow 5_{1,4}$	32180.15	−0.05	−2.35
$5_{1,4} \rightarrow 5_{2,3}$	19197.44	−0.02	1.57
$7_{1,6} \rightarrow 7_{2,5}$	18608.57	0.07	1.87
$8_{1,7} \rightarrow 8_{2,6}$	19002.41	−0.06	0.55
$9_{1,8} \rightarrow 9_{2,7}$	19992.23	−0.12	−2.57
$10_{1,9} \rightarrow 10_{2,8}$	21653.99	0.10	−8.22
$11_{1,10} \rightarrow 11_{2,9}$	24039.08	0.07	−17.12
$13_{1,12} \rightarrow 13_{2,11}$	30995.81	−0.04	−46.14
$8_{2,6} \rightarrow 8_{3,5}$	33248.68	0.03	8.86
$9_{2,7} \rightarrow 9_{3,6}$	31839.96	−0.13	12.53
$10_{2,8} \rightarrow 10_{3,7}$	30459.26	0.17	15.68
$11_{2,9} \rightarrow 11_{3,8}$	29285.39	−0.01	17.25
$12_{2,10} \rightarrow 12_{3,9}$	28497.36	−0.03	15.97
$13_{2,11} \rightarrow 13_{3,10}$	28252.16	−0.06	10.52
$14_{2,12} \rightarrow 14_{3,11}$	28675.71	0.01	−0.46
$15_{2,13} \rightarrow 15_{3,12}$	29860.85	0.01	−18.24

[a] ±0.10 MHz.

then extended to include the *b*-type *Q*-branch $K_{-1}=1\rightarrow2$ and $K_{-1}=2\rightarrow3$ transitions. No *c*-type lines were identified presumably owing to their low intensities produced by a small μ_c. The high *J* *b*-type *P*- and *R*-branch lines were also too weak to be identified. No quadrupole fine structure was observed. The spectrum * is reported in Table 1 and the derived spectroscopic constants are listed in Table 2.

The first excited C−C torsional state was also identified as indicated in Table 2. Searches were made for the second excited state of this mode as well as for the first excited state of the C−N torsional mode, but no assignments could be made presumably because of the weakness of the spectrum.

* The microwave spectra of the vibrationally excited states of conformations I and II are available from the authors upon request or from Molecular Spectra Data Center, Bldg. 221, Room B 265, National Bureau of Standards, Washington D.C. 20234, U.S.A., where they have been deposited.

Rough relative intensity measurements were made for the C−C torsional mode, and a frequency of 140(50) cm⁻¹ was determined. Attempts to calculate the same frequency by assuming the rough force field shown in Table 3 and using the centrifugal distortion constants of Table 2 in the manner described in Ref. 10, were rather inconclusive. A poor fit was obtained, and it is believed that the experimentally determined centrifugal distortion constants are too inaccurate to produce a reliable C−C torsional frequency.

Attempts to measure the dipole moments of both conformations I and II were futile because of insufficient intensities.

Assignment of conformation II. After the completion of the assignment of conformation I, it became clear that at least one further rotamer had to be present. Searches were therefore made for II. This conformation was computed to have $\mu_a=2.2$ D, $\mu_b=2.1$ D and $\mu_c=1.5$ D by the bond-moment method.[9] The strong *b*-type *Q*-branch lines were first identified for this confor-

Table 2. Spectroscopic constants for conformation I of $CH_2NH_2CH_2CN$.[a]

Vibrational state	Ground	First ex. C−C torsion
Numbers of transition	26	16
rms (MHz) [b]	0.0856	0.0872
A_v (MHz)	10526.455(38)	10612.720(97)
B_v (MHz)	3387.403(13)	3374.049(27)
C_v (MHz)	2781.573(13)	2773.412(18)
Δ_J (kHz)	4.11(30)	4.80(41)
Δ_{JK} (kHz)	−22.48(58)	−15.5(17)
Δ_K (kHz)	52.8(60)	−22(24)
δ_J (kHz)	1.313(17)	1.453(46)
δ_K (kHz)	7.20(75)	−1.0(14)

[a] Uncertainties represent one standard deviation. [b] rms is the root-mean-square deviation.

mer. The low J a and b-type R-branch lines were now readily assigned. High J b-type R-branch transitions were then identified by a trial and error procedure amongst lines of suitable intensity with very fast Stark effects. As shown in

Table 3. Assumed diagonal force field,[a] centrifugal distortion constants and torsional frequency for conformation II of $CH_2NH_2CH_2CN$.

Stretching (10^2 Nm^{-1})

C≡N	17.7	H_2C-CH_2	4.4
C−CN	5.2	H_2N-C	5.1
C−H	4.7	N−H	6.4

Bend (aJ rad^{-2})

C−C≡N	0.16	C−C−N	1.3
C−C−C	2.14	H−C−N	0.90
C−C−H	0.66	C−N−H	0.85
H−C−H	0.53	H−N−H	0.47

Torsion (aJ rad^{-2})

C−C	0.11 [b]	C−N	0.25

Centrifugal distortion constants (kHz)

	Obs.	Calc.
Δ_J	4.066	4.084
Δ_{JK}	−22.94	−21.31
Δ_K	66.41	66.51
δ_J	1.2335	1.3327
δ_K	8.33	10.09

[a] See text. [b] Obtained from least-squares fit yielding a C−C torsional frequency of 100(10) cm^{-1} as compared to 140(50) cm^{-1} found by relative-intensity measurements.

Table 4, it was possible to assign 53 transitions with a maximum J of 50. Even higher J transitions were searched for but not identified presumably because of insufficient intensities. No lines split by quadrupole coupling were observed. The frequencies of c-type transitions could be very accurately predicted, but none were found with certainty presumably because of a low c-axis dipole moment component. The spectroscopic constants are listed in Table 5.

Vibrationally excited states of II. Two vibrationally excited states were assigned for conformation II as indicated in Table 5. The strongest excited state which has roughly 50 % of the intensity of the ground state, is presumed to be the first excited state of the C−C torsional mode. Apart from its intensity, the changes of the rotational constants upon excitation are fairly similar to the changes found for conformation I (Table 2). Rough relative intensity measurements yielded 140(40) cm^{-1} for this mode. Force field calculations using the centrifugal distortion constants [10] resulted in a C−C torsional frequency of 100(10) cm^{-1} as shown in Table 3. In this case, a rather good fit was obtained (Table 3) presumably because much more accurate centrifugal distortion constants are available for conformation II than for conformation I.

The second excited state of the C−C torsional mode was searched for and a tentative assignment was made. The rotational constants (not included in Table 5) derived from 8 tentatively assigned lines were: $A=10427.4(16)$ MHz, $B=3348.905(72)$ MHz, and $C=2748.088(81)$ MHz.

Another excited state having about 1/3 of the

Table 4. Microwave spectrum of the ground vibrational state of conformation II of $CH_2NH_2CH_2CN$.

Transition	Observed frequency (MHz)	Obs.-calc. frequency (MHz)	Centrifugal distortion Total (MHz)	Sextic (MHz)
$2_{1,1} \rightarrow 3_{1,2}$	19271.43	0.07	−0.47	
$2_{2,0} \rightarrow 3_{2,1}$	18538.32	−0.02	0.05	
$3_{0,3} \rightarrow 4_{1,4}$	28793.68	−0.04	0.02	
$3_{1,2} \rightarrow 4_{1,3}$	25646.40	−0.01	−1.16	
$3_{2,1} \rightarrow 4_{2,2}$	24858.17	−0.05	−0.50	0.01
$3_{2,2} \rightarrow 4_{2,3}$	24485.43	0.10	−0.26	0.01
$4_{0,4} \rightarrow 5_{1,5}$	33626.88	−0.01	−0.11	0.01
$4_{1,3} \rightarrow 4_{2,2}$	19257.39	0.03	0.68	
$4_{1,3} \rightarrow 5_{1,4}$	31975.05	−0.06	−2.28	0.01
$4_{1,4} \rightarrow 5_{0,5}$	25268.21	−0.11	−2.21	0.01
$4_{1,4} \rightarrow 5_{1,5}$	28974.64	0.12	−0.93	0.01
$4_{2,2} \rightarrow 5_{2,3}$	31279.39	0.00	−1.60	0.01
$4_{2,3} \rightarrow 5_{2,4}$	30558.36	0.02	−0.97	0.01
$6_{1,5} \rightarrow 6_{2,4}$	18114.53	−0.04	1.79	0.01
$7_{1,6} \rightarrow 7_{2,5}$	18060.24	−0.04	1.58	0.02
$7_{1,7} \rightarrow 7_{2,6}$	30489.02	−0.05	−1.65	0.03
$7_{2,5} \rightarrow 7_{3,4}$	33343.95	−0.06	4.65	0.07
$8_{0,8} \rightarrow 8_{1,7}$	22604.14	−0.10	−10.05	0.01
$8_{1,7} \rightarrow 8_{2,6}$	18518.85	0.05	0.22	0.03
$8_{2,6} \rightarrow 8_{3,5}$	32059.29	0.08	8.04	0.10
$9_{0,9} \rightarrow 9_{1,8}$	26970.69	−0.04	−15.35	0.01
$9_{1,8} \rightarrow 9_{2,7}$	19585.86	0.13	−2.90	0.03
$9_{2,7} \rightarrow 9_{3,6}$	30664.24	0.01	11.57	0.14
$10_{0,10} \rightarrow 10_{1,9}$	31683.83	0.09	−21.54	0.02
$10_{1,9} \rightarrow 10_{2,8}$	21335.26	0.13	−8.48	0.04
$10_{2,8} \rightarrow 10_{3,7}$	29323.28	−0.03	14.47	0.18
$10_{4,7} \rightarrow 11_{3,8}$	21179.06	0.03	−36.46	0.03
$11_{1,10} \rightarrow 11_{2,9}$	23815.02	−0.04	−17.19	0.04
$11_{2,9} \rightarrow 11_{3,8}$	28220.71	−0.03	15.69	0.22
$12_{1,11} \rightarrow 12_{2,10}$	27034.30	0.04	−29.41	0.03
$12_{2,10} \rightarrow 12_{3,9}$	27535.45	−0.04	14.00	0.26
$13_{1,12} \rightarrow 13_{2,11}$	30948.18	−0.05	−44.98	0.03
$13_{2,11} \rightarrow 13_{3,10}$	27421.96	0.08	8.12	0.28
$13_{5,8} \rightarrow 14_{4,11}$	22594.21	0.01	−49.90	0.18
$14_{2,12} \rightarrow 14_{3,11}$	28000.98	−0.04	−3.20	0.29
$15_{2,13} \rightarrow 15_{3,12}$	29360.26	−0.05	−21.18	0.27
$16_{2,14} \rightarrow 16_{3,13}$	31552.91	0.02	−46.73	0.22
$18_{7,12} \rightarrow 19_{6,13}$	25554.82	−0.14	−131.53	0.29
$20_{8,13} \rightarrow 21_{7,14}$	23205.12	0.09	−159.32	0.30
$32_{13,19} \rightarrow 33_{12,22}$	25139.29	−0.08	−522.34	1.42
$32_{13,20} \rightarrow 33_{12,21}$	25139.29	−0.11	−522.35	1.42
$33_{13,20} \rightarrow 34_{12,23}$	31577.86	0.04	−622.23	1.83
$33_{13,21} \rightarrow 34_{12,22}$	31577.86	−0.02	−622.24	1.83
$37_{15,22} \rightarrow 38_{14,25}$	27148.45	0.11	−777.76	2.77
$37_{15,23} \rightarrow 38_{14,24}$	27148.45	0.11	−777.76	2.77
$39_{16,23} \rightarrow 40_{15,26}$	24949.86	0.10	−859.23	4.39
$39_{16,24} \rightarrow 40_{15,25}$	24949.86	0.10	−859.23	4.39
$44_{18,26} \rightarrow 45_{17,29}$	26876.36	−0.17	−1204.96	8.04
$44_{18,27} \rightarrow 45_{17,28}$	26876.36	−0.17	−1204.96	8.04
$47_{19,28} \rightarrow 48_{18,31}$	30955.51	−0.02	−1509.95	9.03
$47_{19,29} \rightarrow 48_{18,30}$	30955.51	−0.02	−1509.95	9.03
$49_{20,29} \rightarrow 50_{19,32}$	28723.90	0.07	−1631.58	13.83
$49_{20,30} \rightarrow 50_{19,31}$	28723.90	0.07	−1631.58	13.83

[a] ±0.10 MHz.

Table 5. Spectroscopic constants for conformation II of $CH_2NH_2CH_2CN$.[a]

Vibrational state	Ground	First ex. C−C tors.	First ex. C−N tors.
No. of transitions	53	18	12
rms [b] (MHz)	0.0854	0.091	0.058
A_v (MHz)	10281.375(19)	10353.694(70)	10285.280(66)
B_v (MHz)	3367.7496(43)	3357.962(19)	3373.9074(66)
C_v (MHz)	2761.0828(39)	2754.208(16)	2763.256(11)
Δ_J (kHz)	4.066(38)	2.92(32)	− [c]
Δ_{JK} (kHz)	−22.94(40)	−25.15(85)	−23.27(79)
Δ_k (kHz)	66.41(46)	90(11)	66(10)
δ_J (kHz)	1.2335(71)	1.176(22)	1.249(21)
δ_K (kHz)	8.33(27)	10.28(94)	8.52(80)
H_J (Hz)	0.329(99)	− [c]	− [c]
H_{JK} (Hz)	1.1(18)	− [c]	− [c]
H_{KJ} (Hz)	21.9(35)	− [c]	− [c]
H_K (Hz)	−44.9(74)	− [c]	− [c]

[a,b] Comments as for Table 2. [c] Not fitted. Kept at zero in least-squares fit.

intensity of the ground state was also assigned. Its spectroscopic constants are displayed in Table 5. Relative intensity measurements yielded 210(50) cm^{-1} for this mode. This frequency is typical for an amino group torsional mode.[11] The fact that the changes of the rotational constants upon excitation of this mode are quite small (Table 5), also indicates that this is indeed the first excited state of the C−N torsional vibration.

Searches for further conformations. About 130 transitions were assigned and approximately 10 more lines were tentatively identified as described above. This include all the strongest lines of the spectrum as well as the majority of the transitions of intermediate intensity. Some 20 lines of intermediate intensity could not be accounted for. None of these displayed resolved Stark splittings. Attempts to ascribe these transitions to conformations III, IV, or V of Fig. 1 turned out to be futile.

Predicted rotational constants of III were: A=10.4 GHz, B=3.3 GHz, and C=2.8 GHz. The dipole moment components were predicted [9] to be μ_a=4.2 D, μ_b=2.4 D, and μ_c=1.1 D using the bond-moment method. The unidentified lines could in no way be compatible with the strong a-type R-branch feature predicted for the hypothetical III conformation. The large μ_a predicted for this rotamer lead us to conclude that I and II each are at least 4 kJ/mol more stable than the hypothetical conformation III.

The hypothetical rotamers IV and V are very

nearly prolate tops. A=25.2 GHz, B=2.3 GHz and C=2.2 GHz were predicted for IV, and A=24.5 GHz, B=2.3 GHZ and C=2.2 GHz predicted for V. The a-axis dipole moment components were calculated to be 4.2 D for conformation IV and 3.5 D for V, respectively, using the bond-moment method.[9] The microwave spectra of IV and V should then have strong and simple characteristic pile-ups of the $K_{-1}\neq1$ a-type R-branch transitions. No such simple spectral features were seen. It is again concluded that I and II each are more stable than the hypothetical conformations IV and V by at least 4 kJ/mol. The unassigned lines are then believed to originate from either unidentified vibrationally excited state transitions or impurities.

Energy difference between I and II. Unfortunately, the dipole moment of neither conformation I nor II could be determined, and the values calculated by the bond-moment method [9] and reported above had to be used in order to derive the energy difference between I and II. Intensity comparisons as described in Ref. 12 were made between low K_{-1} a-type R-branch transitions because they are presumed to be very little split by nitrogen nuclei quadrupole effects. The energy difference was found to be zero with a liberally estimated uncertainty limit of ±2 kJ/mol.

Structure. Only one isotopic species was studied for both rotamers and only three rotational constants are thus available for each conformation. A complete geometrical structure cannot,

Table 6. Plausible structural parameters [a] (bond lengths in *pm*, angles in *degrees*) and observed and calculated rotational constants of conformations I and II of $CH_2NH_2CH_2CN$.

Assumed structural parameters common for I and II

$C\equiv N$	115.7	$C-C\equiv N$	180.0	$H-N-C-C$ 60 or 180 from *syn*	
$C-N$	147.5	$C-C-H$	109.5		
$C-CN$	146.3	$C-N-H$	111.0		
$C-C$	154.8	$C-C-C$	110.5		
$C-H$	109.1				
$N-H$	101.7				

Fitted structural parameters

	Conformation I	Conformation II
$N-C-C-C$	63(3) from *syn*	59(3) from *syn*
$N-C-C$	108.0(15)	114.0(15)

Rotational constants (MHz)

Conformation I			Conformation II		
Obs.	Calc.	Diff.(%)	Obs.	Calc.	Diff.(%)
10526.46	10502.44	0.23	10281.38	10289.27	0.08
3387.40	3389.32	0.06	3367.75	3362.23	0.16
2781.57	2789.67	0.29	2761.08	2767.15	0.22

Hydrogen bond parameters

	Conformation I	Conformation II
$H\cdots CN$	255	270
$H\cdots NC$	302	312
$N\cdots CN$	290	298
$N\cdots NC$	366	372
$N-H\cdots C$ [b]	100	98
$N-H\cdots N$ [b]	122	118
$N-H, C\equiv N$ [c]	4	4

Sum of van der Waals radii [d]

$H\cdots C$ [e]	290	$H\cdots N$	270
$N\cdots C$ [e]	320	$N\cdots N$	300

[a] See text. [b] Angles around hydrogen atom involved in hydrogen bonding. [c] Angle between $N-H$ bond involved in hydrogen bonding and cyano group. [d] Taken from Ref. 13. [e] van der Waals radius of carbon assumed to be 170 pm as in aromatic systems.[13]

Table 7. Selected results for some $CH_2XCH_2NH_2$-type molecules involving hydrogen bonding.

X	$\Delta H°$ [a] (kJ/mol)	$\angle X-C-C-N$ (Degrees)	$\angle N-C-C$ (Degrees)	Ref.
NH_2	1.3(8)	63(2) for I and II	109(1) for I; 111.5(10) for II [b]	4
F	0.4(13)	64(2) for I; 63(2) for II	110.0(10) for I; 114.5(10) for II	7
CN	0(2)	63(3) for I; 59(3) for II	108.0(15) for I; 114.0(15) for II	– [c]
OCH_3	<−7.2	61.5(12) for II [d]	112.2(12) for II [d]	6

[a] Positive value for $\Delta H°$ means that I is more stable than II. [b] Average values. [c] Present work. [d] Only II was found.

therefore, be determined for the two rotamers. A selection of parameters to be fitted must be made. The NCCC dihedral angle and the CCN angle were chosen because the rotational constants are sensitive to variation in these chemically interesting parameters and because they are among the structural parameters most prone to change from one conformer to another. In contrast, structural parameters likely to vary among conformers, namely the HNCC dihedral angles as well as the HNH and HNC angles, cannot be accurately fitted because the rotational constants are relatively insensitive to variation in these angles. The amino group was therefore assumed to be in exactly staggered positions in both I and II. Furthermore, the $C-C\equiv N$ angle was assumed to be exactly 180°, even though it is realized that small deviations from linearity normally do occur. The bond lengths and angles, which are shown in Table 6 and kept fixed in the fitting procedure, were taken from recent accurate studies of related compounds.

The dihedral angle NCCC was varied in steps of one degree and the NCC angle in steps of 0.5 degree. The dihedral angles were found as 63(3)° in I and 59(3)° in II, and the NCC angles as 108.0(15)° in I and 114.0(15)° in II, respectively, as seen in Table 6. The error limits have been derived taking into account the inherent uncertainties of the assumed structural parameters.

DISCUSSION

The fact that both conformation I and II each are at least 4 kJ/mol more stable than any other conformation of 3-aminopropionitrile, presumably means that the amino and cyano groups attract each other rather strongly. This attraction is clearly considerably stronger than for thiol and cyano groups as demonstrated in the case of CH_2SHCH_2CN.[14]

The covalent contribution to the hydrogen bonds of the two rotamers of $CH_2NH_2CH_2CN$ must be of minor importance as can be inferred from the hydrogen-bond parameters of Table 6. However, the geometrical arrangement of the $N-H$ bond involved in hydrogen bonding and the cyano groups is very favourable for dipole-dipole interactions in both rotamers because these bonds are about 4° from being parallel in both conformations.

Amines of the $CH_2XCH_2NH_2$ type may possess two hydrogen bonded conformations similar to conformations I and II of Fig. 1. Results for four compounds including $CH_2NH_2CH_2CN$ are collected in Table 7. With the exception of $CH_3OCH_2CH_2NH_2$,[6] conformations I and II are almost equally stable. $CH_2NH_2CH_2CN$ has the NCC angle about 6° smaller in I than in II. Similar results have been found for $CH_2NH_2CH_2NH_2$[4] and $CH_2FCH_2NH_2$[7] as seen in Table 7. The NCC angle is also quite large (112.2(12)°) in conformation II of $CH_3OCH_2CH_2NH_2$ in keeping with the trend seen for the other three molecules of Table 7.

The rather large NCC angles observed for the II conformations of Table 7 are hardly the result of 1,3-repulsion because the non-bonded distance of the hydrogen atoms in question is somewhat larger than the sum of the van der Waals radii. It is also interesting to note that rather large NCC angles have been found for the one identified conformation of $CF_3CH_2NH_2$[1] as well as in conformation III of $CHF_2CH_2NH_2$.[8] In both these two cases, attraction − and not repulsion − between two hydrogen and two fluorine atoms presumably exists. Perhaps the rather large H_2N-C-C angle of II resultts mainly from a slight rehybridization of the carbon atom carrying the amino group and is not a result of repulsion within the molecule.

The heavy-atom dihedral angle XCCN is close to 60° from *syn* in all the molecules of Table 7. It is also characteristic that no heavy-atom *anti* forms have been identified for any of the four molecules in the gaseous state. This points to a rather strong interaction between the amino group and the four proton accepting groups of Table 7. High-temperature electron-diffraction work has been made for $CH_2NH_2CH_2NH_2$ in an attempt to find the heavy-atom *anti* conformation,[15] however, with negative result. It is hoped that such work will be carried out for the remainder of the molecules of Table 7 in order to learn more about the hydrogen bonding ability of the amino group.

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